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Title:	1E30 Cup Cleaning: PETN Compatibility and Freon Substitution by Brulin 815GD
Author(s):	Monroe, Deirdre Christina
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Weapon Systems Engineering Division		
1E30 Cup Cleaning: PETN Compatibility and Freon Substitution by Brulin 815GD		
Number: **W-6-TR-0221U** **LA-UR-**	Revision **A**	Effective Date: **September 5, 2013**

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This document is deemed **UNCLASSIFIED** by:

Dan Borovina, W-6
DC

DLB

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1.0 ABSTRACT

1E30 cup cleaning was done at EG&G Mound using a variety of cleaning agents, including Freon TF (i.e., FC-113). Freon TF is no longer allowed as due to environmental issues and a substitute was sought complex-wide in the mid 1990s. Three cleaning agents were evaluated by Sandia National Laboratories (SNL) and found to be acceptable substitutes for cleaning 1100 aluminum alloy cups. One (Brulin 815D) was determined to be compatible with PETN by Sandia National Laboratories (SNL) based on tests with RR5K PETN. Brulin 815D has been approved for use in cleaning 1E30 cups (9Y121234) dedicated to PETN-based detonators. Compatibility work was planned but not completed for HMX.

2.0 DISCUSSION

Much work has been done over time to find suitable replacements for the Mound use of Freon TF. The most definitive is a 1994 SNL report, MC2990A Detonator Alternate Cleaning Evaluation (Appendix A). Brulin 815GC, Inproclean 1300, and Dirlum 603 were all evaluated and each alternative was superior to Freon TF. SNL planned to evaluate HMX compatibility with Brulin 815D but the work was not completed.

A PETN compatibility study (Appendix B) was done to examine the same cleaning alternatives. None were found to affect PETN based on decomposition exotherms, or other measures.

Table 1 documents key steps of the Mound process (1-12779). Table 2 documents key steps of the Los Alamos National Laboratory (LANL) approach used on the 1E33 PPI and EE lots. Key differences are 1) elimination of Freon TF and an acetone rinse. In addition, the LANL approach adds a 190-proof ethanol rinse after nitric acid passivation. Non-denatured, 190-proof ethanol is compatible with PETN and has been used for decades at Mound with this product.

Table 1. Key steps of the EG&G Mound cleaning process

EG&G Mound 1-12779				
STEP NO.	**OBJECTIVE**	**SOLUTION**	**Sec**	**Times**
1	Clean	Freon TF in ultrasonic cleaner	900	1
2	Rinse	Freon TF (100% FC-113, CFCl2CF2Cl)		3x
3	Rinse	Acetone, Reagent Grade, ACS		1
4	Rinse	Distilled H_20		1
5	Alkaline Etch	15g ACS Grade NaOH + 7.5g ACS Grade NaCO3 + distilled water to make one liter (Solution at 130 to 135 F.	30	1
7	Rinse	Distilled H_20		3
6	Pickle (Passvate)	Nitric (HNO_3) Acid solution (750 ccs of 70% Assay ACS Grade HNO_3)	60	0
8	Rinse	Distilled water		3
3	Rinse	Acetone, Reagent Grade, ACS		3
9	Dry	Heated Air	90 max	0
10	Handling	Plastic Tip Tweezers Only		
11	Packaging	Cleaned Handling Trays		
12	Dimensional Inspect	Random Sample		
13	Post Cleaning Chemical Anal.	Infra-Red Spectroscopy on random sample		
14	Storage	Bonded Stores, Prelabeled containers		

The 1E30 cup cleaning fixture and basket (146Y631262) were developed early on in the 1E33 PPI-2 lot. The cup basket (made from commercially available polyethylene material) was the best alternative examined (among many) in terms of causing the least surface damage to this rather soft aluminum. Other systems had persistent and extensive problems with ultrasonic burning.

A perennial question is "How clean is clean?" One reference considered in early 1E33 lots was a 5/12/86 memo from Rockwell (Appendix C, Cleaning Specifications for Beryllium) that established a $<0.5\mu g/cm^2$ maximum residue level for various contaminants on beryllium. Quantitative standards for cleanliness were not established for early 1E33 lots but further work has been conducted by LANL since that time.

Table 2. Key steps of the LANL cleaning process

LANL DX-1 146Y631258, A				
STEP NO.	OBJECTIVE	SOLUTION	Sec	REP.
1	Clean	Brulin 815GD, 10% by volume to 90 % deionized water. Clean at 52C for 3 minute ultrasonic cycle.	180	1
2	Rinse	Deionized water	10-15	1
3	Passivation	HNO_3 65-75% Assay ACS Grade 200cc HNO_3 to 200 deionized H_2O	50-70	1
4	Rinse	Deionized water	60-90	1
5	Rinse	190-proof Ethanol	60-90	1
6	Dry	UHP Nitrogen	to dry	1
7	Handling	Nylon or Delrin Tipped Tweezers Talc-free latex gloves		
8	Packaging	Cleaned Handling Trays Identifiable containers		
9	Dimensional Inspect	100% dimensional and visual inspection per MD-35076		
10	Post Cleaning Chemical Anal.	None		
11	Storage	Cleaned Handling Tray & Cover		

The Mound cleaning approach did require post-cleaning infrared spectroscopy of a random sample of cleaned cups to verify cleanliness, an excellent practice. The 1E30 cup interior is in intimate contact with high explosive powders over very long periods (i.e., decades) and cleanliness is essential.

3.0 CONCLUSIONS

There is evidence to support use of Brulin 815D as a cleaning substitute for Freon TF in 1E30 (1100 aluminum) cups. There is evidence to support compatibility of Brulin 815D with PETN. There is no direct evidence of HMX compatibility with Brulin 815D and no direct post-cleaning evidence to verify the cleaning efficacy. For both PETN and HMX, direct post-cleaning verification is potentially very valuable.

APPENDIX A

Sandia National Laboratories

Managed and Operated by Sandia Corporation
a subsidiary of Martin Marietta Corporation
Albuquerque, New Mexico 87185-0340

date: 31 October 1994

to: D. E. Hoke, 2653 MS 0326

E.P. Lopez J. A. Ohlhausen

from: E. P. Lopez, 1815 MS 0368 & J. A. Ohlhausen, 1812 MS 0367

subject: MC2990A Detonator Alternate Cleaning Evaluation

Per your request, we have evaluated several alkaline aqueous cleaners as potential replacements for cleaning exploding bridgewire detonators. The EG&G Mound facility has previously had responsibility for producing the MC2990A and other explosive components for the Department of Energy (DOE). They have traditionally used Freon TF for cleaning piece parts that comprise these explosive devices. This technology is currently being transferred to AS-KCD. The production of Freon TF (an ozone depleting chemical) will be discontinued on December 31, 1994. Furthermore, the DOE, AS-KCD and SNL have signed a tri-party agreement restricting the use of ozone depleting chemicals effective July of 1993. Therefore, this is an excellent opportunity to replace Freon TF with an environmentally friendly cleaner. The new cleaner must be capable of removing general machining and handling oils, leave no residue on the cleaned surface, and be compatible with PETN explosive materials. It should clean as well as or better than the existing Freon TF process.

In collaboration with George Bohnert of AS-KCD, we have recommended the following aqueous cleaners for testing: 1) Dirlum 603, Inproclean 1300, and Brulin 815GD. Dirlum 603 has been used at the AS-KCD facility for many years as a general purpose cleaner. Inproclean 1300 has been tested at both AS-KCD and SNL as a potential replacement for mechanical cleaning applications. Brulin 815GD has been tested at SNL as part of an Environmentally Conscious Manufacturing project to clean switch tube assemblies. Gas Chromatography-Mass Spectroscopy (GC-MS) and Auger Electron Spectroscopy (AES) were selected as the methods for determining cleanliness levels. The AES analysis was performed at SNL. This memo discusses AES analysis only. This work was funded under case number S461.120.

Aluminum 6061-T6 detonator barrels were analyzed using AES, after applying different cleaning procedures. Each sample was analyzed using a single spot electron beam on the outside of the barrel. Six sets of samples were analyzed: As received and after cleaning with Brulin 815GD, Dirlum 603, Freon TF (Mound Process), Freon PCA (AS-KCD Process), and Inproclean 1300. Three barrels were analyzed for each of the cleaning processes. The atomic percentages of all surface elemental species were determined using appropriate sensitivity factors. Average values and standard deviations were calculated for each of the cleaning processes.

Many of the samples showed signs of fingerprints, including the common indications of the presence of P, S, Ca, Na and Mg. Any significant combination of these contaminants suggests the presence of human handling. Most of the Mg shown in all scans can be attributed to the 1% Mg (wt%) from the bulk 6061 alloy. The as received set, and both

Freon cleaned sets show signs of fingerprinting. One of the Brulin 815GD samples (highlighted in gray) was significantly worse than the other two Brulin samples. Inappropriate handling may have led to this result and therefore the data from this sample is not used in further calculations. Of the aqueous cleaners (Brulin 815GD, Dirlum 603, and Inproclean 1300), Brulin 815GD and Dirlum 603 leave 1-2% Ca on the surface while Inproclean 1300 leaves about 1% P on the surface as well as segregating bulk Cu from the alloy to the surface (<1%). Significant amounts of Si were noted in all of the samples that were analyzed(~ 10-30%). Silicon is one of the constituents that is found in the bulk of Al 6061-T6 (0.60 wt%). The type of silicon seen on the test samples were not determined. In some cases, Si in the form of silicates can be detrimental to subsequent bonding operations. Overall, Inproclean 1300 cleans the best, while Dirlum 603 and Brulin 815GD are next. All three aqueous cleaners clean better than Freon TF. Both Freon procedures clean equally poorly. The AES results can be seen in Table 1. Other common constituents that are found in Al 6061-T6 are shown in Table 2.

Three alkaline aqueous cleaners were tested for cleaning exploding bridgewire detonators as potential replacements for Freon TF. Auger analysis indicates that all three cleaned better than Freon TF. Overall, Inproclean 1300 cleaned the best, however, Brulin 815GD is also a satisfactory replacement. Dirlum 603 is not recommended for further evaluation because of its high pH value of 12.5, which makes it a RCRA waste. Compatibility of the recommended cleaners with explosive PETN and other materials that comprise the detonators should be considered next.

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George Bohnert Dept. 834 MS2C43

Table 1 - AES Re......(Surface Contaminants at %)

AUGER Analysis on MC2990A Detonator Parts

Cleaner		P	S	Cl	C (If C large, Ca is masked.)	Ca	N	O (Cr masked by O)	F	Cu	Na	Mg	Al	Si
As Recieved	Sample 1	0.00%	0.04%	0.00%	60.82%	0.00%	0.35%	9.81%	0.96%	0.00%	0.98%	1.41%	15.01%	10.62%
As Recieved	Sample 2	0.00%	0.00%	0.00%	67.87%	0.00%	0.53%	6.81%	0.84%	0.00%	0.81%	0.91%	8.22%	14.01%
As Recieved	Sample 3	0.00%	0.06%	0.00%	42.65%	0.00%	0.40%	16.26%	1.15%	0.00%	0.24%	1.48%	19.02%	18.75%
Average		0.00%	0.03%	0.00%	57.11%	0.00%	0.43%	10.96%	0.98%	0.00%	0.68%	1.27%	14.08%	14.46%
Std Dev		0.00%	0.03%	0.00%	13.01%	0.00%	0.09%	4.83%	0.16%	0.00%	0.39%	0.31%	5.46%	4.08%
Brulin 815GD	Sample 1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.71%	14.81%	0.61%	0.00%	[illegible]	2.11%	16.17%	15.43%
Brulin 815GD	Sample 2	0.00%	0.00%	0.00%	4.47%	2.07%	0.00%	33.38%	0.64%	0.00%	0.00%	1.12%	32.17%	26.15%
Brulin 815GD	Sample 3	0.00%	0.00%	0.00%	3.21%	2.16%	0.00%	33.71%	0.63%	0.00%	0.00%	0.93%	30.10%	29.26%
Average		0.00%	0.00%	0.00%	3.84%	2.12%	0.00%	33.55%	0.63%	0.00%	0.00%	1.02%	31.13%	27.70%
Std Dev		0.00%	0.00%	0.00%	0.89%	0.07%	0.00%	0.24%	0.01%	0.00%	0.00%	0.13%	1.46%	2.20%
Dirlum 603	Sample 1	0.00%	0.11%	0.00%	2.46%	1.08%	0.25%	28.60%	0.14%	0.00%	0.00%	1.96%	46.52%	18.87%
Dirlum 603	Sample 2	0.00%	0.08%	0.03%	1.39%	1.24%	0.18%	30.67%	0.11%	0.00%	0.00%	1.81%	50.76%	13.75%
Dirlum 603	Sample 3	0.00%	0.08%	0.00%	2.06%	1.43%	0.00%	29.80%	0.00%	0.00%	0.00%	1.80%	49.00%	15.83%
Average		0.00%	0.08%	0.01%	1.97%	1.25%	0.14%	29.69%	0.08%	0.00%	0.00%	1.86%	48.76%	16.15%
Std Dev		0.00%	0.02%	0.02%	0.54%	0.17%	0.13%	1.04%	0.07%	0.00%	0.00%	0.09%	2.13%	2.57%
Freon (Mound)	Sample 1	0.59%	0.44%	0.02%	48.09%	0.08%	0.59%	13.02%	1.02%	0.00%	1.47%	2.42%	23.15%	9.09%
Freon (Mound)	Sample 2	0.21%	0.64%	0.11%	50.11%	0.00%	1.02%	12.24%	1.18%	0.00%	1.74%	2.70%	22.02%	8.02%
Freon (Mound)	Sample 3	0.00%	0.10%	0.00%	45.67%	0.08%	0.27%	14.69%	0.96%	0.00%	0.24%	2.15%	26.47%	9.37%
Average		0.27%	0.40%	0.04%	47.96%	0.05%	0.63%	13.32%	1.05%	0.00%	1.15%	2.43%	23.88%	8.83%
Std Dev		0.30%	0.27%	0.06%	2.22%	0.04%	0.37%	1.25%	0.11%	0.00%	0.80%	0.28%	2.32%	0.71%
Freon PCA	Sample 1	0.05%	0.02%	0.00%	53.71%	0.00%	0.77%	11.03%	0.52%	0.00%	0.07%	1.39%	22.20%	10.24%
Freon PCA	Sample 2	0.50%	0.03%	0.00%	42.93%	0.07%	1.12%	15.78%	0.45%	0.00%	0.10%	1.52%	26.88%	10.65%
Freon PCA	Sample 3	0.22%	0.07%	0.00%	50.95%	0.00%	0.55%	12.96%	1.04%	0.00%	0.39%	1.46%	23.53%	8.84%
Average		0.25%	0.04%	0.00%	49.20%	0.02%	0.81%	13.26%	0.67%	0.00%	0.19%	1.46%	24.20%	9.91%
Std Dev		0.23%	0.02%	0.00%	5.60%	0.04%	0.29%	2.39%	0.32%	0.00%	0.18%	0.07%	2.40%	0.95%
Isproclean1300	Sample 1	0.96%	0.12%	0.00%	4.64%	0.00%	0.31%	28.49%	0.00%	1.24%	0.07%	0.59%	59.34%	4.24%
Isproclean1300	Sample 2	0.77%	0.12%	0.00%	7.32%	0.00%	0.49%	28.23%	0.00%	0.28%	0.00%	0.83%	49.95%	12.03%
Isproclean1300	Sample 3	0.82%	0.12%	0.00%	6.99%	0.00%	0.31%	28.32%	0.00%	0.72%	0.00%	0.91%	57.02%	4.78%
Average		0.85%	0.12%	0.00%	6.32%	0.00%	0.37%	28.35%	0.00%	0.75%	0.02%	0.78%	55.44%	7.01%
Std Dev		0.10%	0.00%	0.00%	1.46%	0.00%	0.10%	0.13%	0.00%	0.48%	0.04%	0.17%	4.89%	4.35%

Table 2 - Al 6061 - T6 Constituents (wt%)

Al = 97.90
Si = 0.60
Cu = 0.28
Mg = 1.00
Cr = 0.20

APPENDIX B

Sandia National Laboratories

Albuquerque, New Mexico 87185-0329

date: April 17, 1995

to: D. E. Hoke, Dept. 2653, MS 0326

T. M. Massis R. T. Patton

from: T. M. Massis and R. T. Patton, Dept. 2652, MS 0329

subject: Compatibility of PETN and Aqueous Alkaline Cleaning Agents

Compatibility studies of PETN with various aqueous alkaline cleaning agents have been completed for potential use in your detonator applications. The following aqueous alkaline cleaning agent were evaluated (Table 1). Samples were obtained from E. P. Lopez, Department 1815. The PETN used in these studies was Mound production RR5K powder.

Table 1
Aqueous Alkaline Cleaning Agents Studied

1. Inpro Clean 1300 (10% in DI water)
2. Brulin 815GD (10% in DI water)
3. Dir L-Lum 603 (28 grams/liter in DI water)

Table 2 lists the analytical testing procedures used to perform these compatibility studies.

Table 2
Compatibility Analytical Procedures

1. Differential Scanning Calorimetry (DSC)
2. Accelerating Rate Calorimetry (ARC)
3. Chemical Reactivity Test (CRT)

Differential Scanning Calorimetry (DSC)

The DSC thermal analysis procedure involved mixing equal quantities of PETN with one of the aqueous alkaline cleaning agents and placing it in a gold sample pan which was then sealed. Gold was used because of the possible reactivity of the high pH cleaning agent with aluminum sample pans that are normally used. The samples were then dynamically heated at a rate of 10°C/minute in a TA Instruments Model 2200 thermal analysis system until the reaction or decomposition exotherm was completed. These data were then compared to similar DSC data for individual samples of the aqueous cleaning agent and RR5K PETN. Shifts in the transitions, primarily the decomposition exotherm of the PETN, were noted.

For the mixtures of the aqueous alkaline cleaning agents and PETN, no shifts in the mixture exotherms when compared to the individual materials were measured. The adiabatic decomposition exotherm intensity for the mixtures was suppressed considerably when compared to PETN by itself. Note that the aqueous alkaline cleaners did not exotherm appreciably over the temperature range tested-300°C.

By the ARC procedure, these aqueous alkaline cleaning agents are considered compatible with PETN.

Chemical Reactivity Test (CRT)

The Chemical Reactivity Test (CRT) procedure involves aging equal quantities of the cleaning agent in question and PETN in a valved, stainless steel container at an isothermal temperature of 70°C for a seven day time period. Separate individual samples of the cleaning agent and PETN are similarly aged. After aging, the CRT container is attached to a gas chromatograph, the valves opened and the gaseous contents, including any evolved gases, swept onto the gas chromatograph column for separation and analysis. The evolved gas data from the mixtures in question are compared to evolved gases from the individual samples and an evaluation of compatibility made.

Criteria for reaction or potential incompatibility are an increase in total gas volume of 3-5 times of the mixture compared to the sum of the individual materials <u>and</u> an evolved gas volume of the mixture greater than 100 microliters after the individual gas volumes have been subtracted. Typical evolved gases that are used for compatibility criteria include oxygen, nitrogen, nitrous oxide, nitric oxide, carbon dioxide and carbon monoxide, Water is analyzed for information purposes only because of adsorbed moisture on the stainless steel aging fixture that can never be totally removed prior to loading. Note, that for these aqueous alkaline cleaning agents, large quantities of water were evolved since they were water based and the samples were 50/50 (PETN/cleaning agent) weighing 200 milligrams each. Other gases, such as organics and sulfur containing gases, can also be analyzed if present.

For the three aqueous alkaline cleaning agents tested with PETN, no incompatibility by the CRT method was found. The total gas volumes was nearly zero with a ratio of one for gas the volumes of evolved gases compared to the individual materials. No reaction gases, such as nitrous oxide or nitric oxide, from the PETN were measured.

Conclusion

No compatibility problems with PETN and the three aqueous cleaning agents listed in Table 1 were found with the DSC, ARC and CRT analytical procedures used. They can be considered compatible with PETN. There was no advantage of one cleaning agent over the others in regard to compatibility. All three gave similar results.

Long term tests are still being planned but will not start until the move to the new Explosives Components Facility (ECF) is completed. Do not expect the long term compatibility testing to start before August, 1995.

A comprehensive report will be written once the CRT data are completed for the three cleaning agents in Table 1 and the explosives HNS, HNAB and HMX. These tests will be completed prior to the ECF move which is scheduled to start in early May, 1995

Distribution:
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MS-0637 G. E. Dahms (Dept. 12336)
MS-0329 Day File (Dept. 2652)

APPENDIX C

most UB line
2 pgs

Scanned in MTL Database
5/2/01 Tech
Initial

IRF Record

Internal Letter **Rockwell International**

Date May 12, 1986

No. PSD86-031

TO (Name, Organization, Internal Address)

L. E. Wilson
W80/ASW Program Mgmt
Building 750

FROM (Name, Organization, Internal Address, Phone)

J. L. Briggs
Chem Proc Sys Dev
Building 881
4925

SUBJECT: CLEANING SPECIFICATIONS FOR BERYLLIUM

Aqueous detergent cleaning has been employed at Rocky Flats Plant for 12 years and has provided excellent final cleaning results for beryllium WR parts. At your request, a summary of the cleanliness specifications for surface residues has been prepared for qualifying prospective offsite beryllium contractors.

The standard aqueous detergent ultrasonic cleaning process for beryllium WR parts is specified by Rocky Flats document M-10522 and consists briefly of the following:

1. Ultrasonic clean in 2 vol % Oakite NST detergent for 5 minutes at $50 \pm 5^{\circ}C$.

2. First rinse in cascading deionized water for 5 minutes minimum at ambient temperature.

3. Second rinse in cascading deionized water for 5 minutes minimum at ambient temperature.

4. Warm air dry for a minimum of 5 minutes.

The deionized rinse water and detergent make-up water must conform to ASTM Type IV standard purity specifications. Maximum allowable residue levels specified for final cleaned beryllium parts are summarized in Table I.

The maximum acceptance for contaminated surface residues in Table I were established by compiling residue data from numerous aqueous detergent cleaning studies. A statistical evaluation was then performed that provided the upper limit residue levels in Table I for cleanliness standards(1) at Rocky Flats Plant.

Patent Reviewed
7-3-86
RL Leggett

"REVIEWED FOR CLASSIFICATION
By [signature] (U)
Date 5/12/86"

L. E. Wilson
May 12, 1986
Page 2

TABLE I

Maximum Surface Residue Levels for Final Cleaned Beryllium Parts[1]

Residue Type	Maximum Residue ug/in²	µg/cm²	Analytical Method[a]
Nitrate (NO_3^-)	<3.0	<0.5	Ion Chromatography
Chloride (Cl^-)	<3.0	<0.5	Ion Chromatography
Sulfate (SO_4^{-2})	<3.0	<0.5	Ion Chromatography
Phosphate (PO_4^{-3})	<3.0	<0.5	Ion Chromatography
Fluoride (Fl^-)	<3.0	<0.5	Ion Chromatography
Hydrocarbon (C-H)	<11.0	<2.0	Infrared Spectroscopy
Cations (Metal elements, e.g. Fe, Si, Na)	<3.0	<0.5	Ion Coupled Plasma Spectroscopy

(a) Residue determinations by analytical rinses.

Offsite vendor cleaning facilities must be approved by Rockwell International, Chemical Process Systems Development group at the vendor facility.

J. L. Briggs
J. L. Briggs
Chemical Process Systems Development

cc:
F. B. Baker
B. T. Cross
T. L. Rising
IRF (Record)

REFERENCE

1 D. A. Greer, Statistical Applications, "Residue Analysis", Rockwel International, Rocky Flats Plant, August 16, 1984.